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<b>(21) International Application Number:</b> PCT/EP94/00633 <b>(22) International Filing Date:</b> 4 March 1994 (04.03.94)  <b>(30) Priority Data:</b> 9304521.9                      5 March 1993 (05.03.93)                      GB  <b>(71) Applicant (for all designated States except US):</b> EXXON CHEMICAL PATENTS INC. [US/US]; 1900 East Linden Avenue, Linden, NJ 07036 (US).  <b>(72) Inventors; and</b> <b>(75) Inventors/Applicants (for US only):</b> FOLIE, Bernd [BE/BE]; 16, avenue de la Paix, B-1640 Rhode-Saint-Genese (BE). BARON, Norbert [DE/DE]; Heinrich-Hoerle-Strasse 4, D- 50735 Koeln (DE).  <b>(74) Agents:</b> VELDHUIZEN, Albert, Dirk, Willem et al.; Exxon Chemical Limited, Exxon Chemical Technology Centre, P.O. Box 1, Abingdon, Oxfordshire OX13 6BB (GB).		<b>(81) Designated States:</b> US, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> IMPROVED ALUMOXANE, METHOD FOR ITS PREPARATION AND POLYMERISATION PROCESS USING SUCH ALUMOXANE  <b>(57) Abstract</b>  The invention provides a method of subjecting an alumoxane to a secondary hydrolysis which comprises: hydrolysing an alumoxane starting solution which is macroscopically substantially clear and has a viscosity approximating that of the solvent and a content of a Al containing compounds of at least 3 wt % in such a manner as to produce a substantially stable, opaque suspension having a viscosity at least 0.1 centistoke preferably 0.2 centistoke above that of the starting solution.		

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Improved alumoxane, method for its preparation and polymerisation process using such alumoxane

Field of invention:

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The invention relates to an improved alumoxane, methods for the preparation of such alumoxanes and also to polymerisation processes using such alumoxanes. Alumoxanes can be used for example as cocatalyst components particularly but not  
10 exclusively in conjunction with a transition metal component containing a pi-bonded moiety such as a cyclopentadienyl compound. The term cyclopentadienyl compound is used herein to indicate a compound in which a metal atom is bonded through one or more pi-bonds to one or more mono or polynuclear  
15 moieties containing an unsaturated five-membered carbon ring.

The polymerisation may be performed with monomers capable of addition polymerisation including ethylene, propylene, other higher alpha olefins, polyenes such as dienes and also  
20 aromatic and other cyclic compounds capable of addition polymerisation, such monomer generally having up to 20 carbon atoms.

The polymerisation process may use the alumoxane in supported or unsupported form depending on the process variant. The  
25 alumoxane may be particularly used for processes where the polymer is present in fluid form such as high pressure polymerisation processes and the alumoxane is unsupported.

30 Background of the invention :

In numerous prior published patent documents an alumoxane, in particular methylalumoxane (MAO), is described as the cocatalyst to be used side-by-side with a transition metal  
35 compound such as a metallocene for use in olefin polymerisation by a number of process routes. Generally the patent literature represents alumoxane as an oligomer obtained by the partial hydrolysis of an aluminum trialkyl. Cyclic and

linear structural formulae have been disclosed (See BASF EP 35242). The degree of oligomerisation varies. This is generally determined simply from a molecular weight determination which is now understood to give an average  
5 molecular weight as most alumoxane preparations contain a variety of species of different molecular weight.

Opinions have varied as to what characteristic gives the most effective alumoxane when used with any particular metallocene.  
10 The overall consensus appears to be that high average molecular weights aid cocatalytic activity.

For example, in the thesis of Klaus Kuelper, 1985 Hamburg University, page 62 the oligomerisation degree is seen as the  
15 decisive factor : low molecular weight, still liquid hydrolysates of trimethylaluminum (TMA) have low or no activity in olefin polymerisation. Highest activity is obtained using high molecular weight AO structures. In a thesis by Rüdiger Woldt, 1982, Hamburg, page 111, the aluminum  
20 component is seen as the weakness of the catalyst system.

The precise chemical structure of alumoxanes is unclear. Considerable studies have been completed to elucidate the structure, presumably to help select the optimum alumoxane  
25 species. Lasserre and Derouault in Nouveau Journal de Chemie, Vol. 7 N 11-1983, p 659 identified an association-dissociation process between the different alumoxane species. Giannetti, Nicoletti and Mazzochi in the Journal of Polymer Science Polymer Chemistry edition Vol. 23 2117 -2133(1985)  
30 also conclude that highest activities are obtained by alumoxane cocatalysts having a high degree of oligomerization. Sinn, Bliemeister, Clausnitzer, Tikwe, Winter and Zarncke in a report on a Symposium on Transition Metals and Organometallics as Catalysts for Olefin Polymerisation published by Springer  
35 Verlag 1988 discuss the presence of trimethyl aluminum in the hydrolyzed product and the manner of its association. All

this clearly illustrates the difficulty of closely identifying the best alumoxane for polymerisation purposes.

5 M. Pasyнкiewicz in Polyhedron Vol. 9 No 2/3, pp 429-453 suggests that the amount of free trimethylaluminum present influences the solubility of methylalumoxane; the higher the amount the more soluble.

10 The published art including that referred to above describes various ways of making alumoxane repeatedly and in detail. It is reasonable to expect that depending also on the precise reaction conditions these methods will produce alumoxanes of different type, possibly with varying effect on the polymerisation. In many of the methods toluene is used as the  
15 solvent. Where clear solutions are reported or prepared possible insoluble materials are removed or avoided. This may have impact on the oligomerisation degree for example. Thus the method used not only affects the yield etc. but also the nature of the alumoxane.

20

Nearest art on this subject :

The art not only illustrates the variety of variables in the preparation and in the structural and compositional features  
25 but also that, apart from molecular weight, there is no accepted correlation between these features and polymerisation performance.

30 Alumoxanes are mostly reported to be produced by hydrolysing a trialkyl aluminium, especially trimethylaluminium (TMA) with water in a solvent such as toluene. Hydrolysis ratios ( $H_2O:Al$ ) in these systems vary.

35 The Lasserre and Derouault article above suggests ratio's between zero and one because greater values lead to gel formation. It records a preferred range of 0.3 to 0.5.

Hydrolysis is said to progress preferably by reaction of the already hydrolysed species involving the reaction of water with low molecular weight MAO species.

5

In EP 108 339 a hydrolysis ratio of  $H_2O:Al$  of 1:0.52 (equivalent to 1.9:1) is used until 1 Mol of methane has developed. Methylalumoxane (MAO) is obtained in a yield of 63 %. In Example 1, the material has a cryoscopic molecular weight of 1170 and a degree of oligomerisation of 20.

In EP 299 391 MAO is prepared using a hydrolysis ratio of 0.475:0.25 (=1.9) until 2-3 mol of methane has developed per mol of TMA in Example 1. The molecular weight was 710.

15

In EP 315 234, Example 3 a two step procedure is used. It starts in a first step with MAO prepared from TMA (1.15 mol) and is combined with 0.6 mol of water absorbed on aluminium hydroxide in toluene giving a hydrolysis ratio of 0.52 until 1 mol of methane evolved per mol TMA. Supernatant liquid was removed from solids. In a second step more water absorbed on aluminium hydroxide is added corresponding to 0.37 mol of water. Another amount of methane evolved corresponding to 0.73 mol relative to the original TMA added. The solids were allowed to settle. The supernatant presumably contains dissolved MAO.

In EP 200 351 Example 16 uses a hydrolysis ratio ( $H_2O : Al$ ) of 0.87:0.5 (=1.74) to produce a molecular weight of 2800 (oligomerisation degree of 46).

In EP 328 348 a two step procedure is used. In Example 1, in the first step a hydrolysis ratio ( $H_2O : Al$ ) of 1.74 is used to produce MAO in toluene. The solids were filtered. Toluene was removed from the filtrate to give 12 g of MAO as a white solid. This is redissolved in toluene. The molecular weight

is 870. The yield of MAO can be calculated to be below 30 %. In a second step the MAO was added to a vessel containing water in toluene to give a hydrolysis ratio of 0.5:5 (=0.1). An improvement in yield and molecular weight results.

5

In EP 360 492 the first step is the same, but in a second step the MAO is treated with water at a hydrolysis ratio calculated at 0.4. This material is filtered again; presumably the solid this time is a benzene insoluble organo-aluminium oxy-compound.

10

In the thesis of Heinrich Haehnsen, 1985, Hamburg University high molecular weight alumoxanes are preferred (page 3/4). Page 83 onwards discusses the synthesis of MAO. On page 105 reference is made to the development of insoluble MAO residues (R). Page 123 onwards discusses MAO analysis. Page 167 considers a possible conclusion that fully hydrolysed, strongly acid "AlO<sub>3</sub>" centres are very significant and that their heterogenising influence only permits small amounts of soluble MAO. To increase the content of AlO<sub>3</sub> centres subsequent treatment is suggested (in the vapour phase, by moist solvent or even directly). The author however expects a reduction in homogeneity.

15

20

Given the considerable excess of alumoxane required for good polymerisation activity and given the cost of TMA there is also a need to produce the alumoxane using large scale processes in which processes the precise reaction conditions may not be controllable in detail and be subject to process variations associated with larger scale operation.

25

30

There is hence also a need to use industrial scale processes to produce low cost alumoxane of reproducible quality and performance. More particularly there is a need for a process that does so without undue separation, removal and wastage of

35

low activity components, and which produces a highly active form of alumoxane.

5 Summary of the invention

In the invention a slow, gradual, even hydrolysis is used to drive the alumoxane hydrolysis to a clearly definable end point. The starting alumoxane to be driven to the hydrolysis  
10 end point can be selected for stability and cost etc. whilst the alumoxane which has been brought to the end point can have a predeterminable impact on polymerisation. The starting materials, processes and products can, by their nature, vary considerably but this specification describes the details to  
15 the extent that the nature of the invention so permits.

The secondary hydrolysis

The invention provides firstly a method of subjecting an  
20 alumoxane to a secondary hydrolysis which comprises hydrolysing an alumoxane starting solution or suspension which has a nominal concentration of 3 wt% Al, and has an initial viscosity, generally approximating that of the solvent in such a manner as to produce a substantially stable suspension  
25 having a final viscosity at least 0.1 preferably 0.2 centistoke above the initial viscosity.

With the nominal concentration is meant an alumoxane starting solution whose concentration is adjusted for viscosity  
30 measurement purposes to 3 wt% Al. The hydrolysis and polymerisation proper may of course employ solutions of higher or lower Al concentration but the viscosity change can be normalised for the purpose of detecting conformity or not with the invention to a standardised 3 % solution.



The Al content refers to total content of Al including compounds, alumoxane precursors of alumoxane and any overhydrolysed products.

- 5 The viscosity can be measured according to ASTM-D-445 : The viscosity of a solution of nominal concentration increases preferably exceeds 0.2 centistoke, especially 0.5 centistoke. The concentration can be as low as 1 % Al but is preferably from 4 to 10 wt% but may be up to 30 or 40 wt% or higher. At
- 10 higher concentrations, the viscosity increase is more pronounced. The viscosity increase may then be in excess of 1 centistoke and/or be double that of the alumoxane starting solution. The hydrolysis also leads to a reduction in TMA content of the solution or suspension.
- 15
- The final viscosity should be measured immediately upon completion of secondary hydrolysis because ageing can lead to variations in viscosity.
- 20 The term "approximating that of the solvent" indicates that the viscosity is little higher. Typically toluene has a viscosity of 0.72 centistokes; a 3 wt% Al containing hydrolysate of trimethylaluminum and water, which is transparent has a viscosity of 0.9.
- 25
- The difference between the final viscosity and the initial viscosity preferably exceeds the difference between the initial viscosity and the viscosity of the solvent on its own.
- 30 Preferably the viscosity increase should be limited to less than 20 centistokes, especially less than 3 centistokes for a solution normalised to 3wt % of Al. Also the final suspension should be free of gels so that more than 90 % preferably more than 95 % of the Al component present passes a filter having a
- 35 pore size of less than 0.5 preferably less than 0.1 mm.

A suitable manner of hydrolysis leads at the end point to the desired micro suspension with elevated viscosity. It is believed that an appropriate increase in viscosity is in fact indicative of MAO of a desirable composition and structure  
5 from the point of view of cocatalytic activity.

The manner of hydrolysis, desirable to provide the viscosity increase, is generally slow and controlled. Different temperatures and water addition methods may be used but local  
10 steep gradients in water concentration should be avoided, to avoid formation of excessive solids or gels exceeding 0.5 to 1 mm diameter. In the later section "details of secondary hydrolysis", general process boundary conditions are set out which include features which have not been used in prior art  
15 processes. The Examples include a comparison of the effect of no, slow and fast hydrolysis and provides general guidance.

The extent of hydrolysis achieved at the end-point of the method of the invention can vary and is optimised by reference  
20 to polymerisation performance. In the later section "details of the hydrolysis product" ranges are given of general product characteristics. Examples are included which illustrate how optimum hydrolysis levels are determined.

It has surprisingly been found that the viscosity change provided by the method of the invention can be created in commercially available MAO solutions by an appropriate degree and manner of hydrolysis. Suitably it should be performed gradually and slowly. It has also been found that the  
25 viscosity change leads to much improved polymerisation performance.  
30

The starting solution may be obtained by any form of primary hydrolysis or other alumoxane preparation method. In some  
35 primary hydrolysis methods used in the art, water is used at a level which produces alumina-like gels or solids which are

removed (See EP 315 234). The term "solution" is used herein to include solutions containing a low level of macroscopically visible solids or gels which can settle out on storage and which do not significantly influence the transparency of the solution.

The change in viscosity results from the secondary, preferably slow, hydrolysis.

It is believed that the change in the physical condition from a low viscosity solution to a higher viscosity suspension corresponds to a reduction in unreacted aluminum alkyl and low oligomers relative to high oligomers and possibly alumina-like solids. The change is on balance highly beneficial to the catalytic activity. The invention also permits stable solutions to be prepared in bulk, stored and shipped whilst a secondary hydrolysis at the site of polymerisation causes the alumoxane to be optimised to a predictable efficient performance level. It is believed that the TMA (unreacted aluminum alkyl) may act to stabilise the solution.

The invention secondly provides a stable, opaque suspension of an alumoxane in a solvent medium said suspension having a viscosity of from 1 centistoke to 10 centistoke, preferably from 1.1 to 7 centistoke, when normalised to a concentration of 3 wt% Al.

It is furthermore a surprising benefit that optimum secondary hydrolysis levels can be determined to provide reproducible polymerisation conditions from different batches of commercially supplied MAO. Such different batches might otherwise have quite varying cocatalytic effect.

The end point for the hydrolysis in the method of the invention and so the extent of secondary hydrolysis can be varied and the residual unhydrolysed aluminum alkyl can be

measured by titration. References to "unreacted aluminumalkyl" herein are references to the material whose presence can be determined by titration. The performance in polymerisation can then be tested. For a given polymerisation process an optimum performance level can be achieved by using the secondary hydrolysis to give the particular residual unreacted aluminum alkyl level associated with the optimum performance, in other words the residual aluminum alkyl may be used as an indicator to determine the end point of the secondary hydrolysis.

The term "secondary" in hydrolysis is used for convenience on the assumption that generally MAO results from hydrolysis but there is no overriding requirement that a primary hydrolysis be performed. There are some ways of producing MAO without hydrolysis. Such alumoxanes are also described as undergoing a secondary hydrolysis for the purpose of the invention as long as a substantially clear alumoxane solution is involved as a starting material.

#### Details of the primary hydrolysis

The starting material is generally produced by a primary hydrolysis although any method producing a substantially clear alumoxane solution would be suitable as indicated above.

The primary hydrolysis may be by any method known in the art. Patent references include:

- EP 371 084 uses ice erosion in a solution;  
EP 338 044 uses a porous imbibing material containing absorbed water;  
EP 315 234 is similar to EP 338 044;  
EP 372 483 uses a T-shaped reactor and a hydrocarbon solvent with water in a distinct phase.

- EP 388 630 uses a counter-flow column;  
EP 403 830 uses a low temperature and water containing atmosphere;  
EP 405 221 uses a vigorously agitated multi-stage reactor system.  
5

Various other techniques are described in :

- EP 108 339 aluminum sulphate hydrate is used;  
10 EP 299 391 produces a "cross-linked" structure by stepping the reaction having regard to the amount of alkane formed;  
EP 383 255 uses a solvent system;  
EP 393 358 is similar to EP 383 255;  
15 EP 399 384 is based on a drying process for a viscous solution using shear;  
JP 3074 410 uses repeated condensation;  
EP 258 924 uses ultrasonic dispersion;  
EP 257 695 uses a high speed shear impeller;  
20 EP 372 617 uses tetra-alkyl dialumoxane as a starting material;  
JP 2247 201 uses two types of aluminum alkyl. Specific mention is made of n-octyl derivatives  
JP 2250 805 uses aliphatic solvents as a hydrolysing medium;  
25 EP 317 955 uses a system providing an immediate dispersion of water on contact with an aluminum alkyl solution.
- 30 Generally speaking an aluminum alkyl is hydrolysed in a solvent with water in a manner to control the exothermic reaction, suitably by delivering the water to the system gradually and /or at low temperatures, advantageously in conditions to provide homogeneous contact conditions.
- 35 Preferentially free water should be added in the absence of a crystalline or absorbent carrier.

The aluminum alkyl may include trimethyl aluminum (TMA), triethyl aluminum, or other C<sub>1</sub> to C<sub>20</sub> hydrocarbyl, particularly alkyl derivatives. At least two kinds of aluminum alkyls may be used as in JP-2247201-A (Toyo Stauffer). Halogenated aluminum alkyls are also included.

The solvent is preferably an aromatic solvent such as toluene but it may also be an aliphatic solvent preferably a C<sub>5</sub>-C<sub>12</sub> such as heptane.

10

As indicated above, commercially produced alumoxane material should be substantially homogeneous for storage and shipping stability.

15 The alumoxane produced by primary hydrolysis may have the following characteristics:

concentration based on total aluminum : 2 to 50 %, preferably 5 to 30 % wt %; content of unreacted aluminum alkyl : 10 to 50  
20 %, preferably 15 to 30 mol % of total aluminum (based on titration method); molecular weight by cryoscopy : 500 to 5000, preferably 800 to 1500; and average degree of oligomerisation is obtained by dividing the molecular weight by 58.

25

The titration methods for determining the concentration of total Al including unreacted aluminum alkyl can follow the methods described in E. Wänninen and A. Ringbom, "Complexometric titration of aluminum", *Analytica Chimica Acta*  
30 12, 308 (1955); F. Nydal "The indirect Complexometric Titration of Aluminum : A study of the Wänninen-Ringbom Method" *Talanta*, 4, 141 (1960) D.F. Hagen, B.G. Biechler, W.D. Leslie, and D.E. Jordan "Controlled deactivation-hydrolysis and determination of aluminum in aluminum alkyl compounds",  
35 *Analytica Chimica Acta*, 41, 557 (1968).

The amount of unreacted aluminum alkyl can be determined by a separate test as set out for example in :

- E. Bonitz, Chemische Berichte 88, 742 (1955);  
5 K. Ziegler et al. Liebigs Ann. Chem. 629, 20 (1969); and  
G.A. Razuvaev and A. Graevskii Doklady Akad. Nauk, SSSR 128,309 (1959)

- 10 These methods can be adapted for the selective titration of free unreacted aluminum alkyl that is to say aluminum alkyls which will dissociate from the alumoxane in an appropriate solvent.

#### Details of the secondary hydrolysis

15

- The secondary hydrolysis is preferably performed gradually and progressively to avoid excessive water concentration gradients during the hydrolysis and ensure that the water in the system is always dissolved at a molecular level avoiding localised  
20 hydrolysis which could lead to insoluble species (gels or solids). Agitation is hence generally desirable. The solution / suspension may become more or less opaque as hydrolysis progresses particularly at higher Al concentrations.

25

The secondary hydrolysis is preferably performed as follows:

- The duration should generally be from 1 to 48 hours, preferably 2 to 24 hours especially 4 to 20 hours; the  
30 temperature should generally be from -20°C to 90 °C, preferably 20 to 70 °C and especially 20 to 40 °C Lower temperatures facilitate gradual hydrolysis. The temperature and duration should be selected to limit volatilisation of aluminum alkyl such as TMA if the process is performed under  
35 atmospheric, unpressurised conditions. Preferably the temperature is increased gradually from 40 to 80°C.

The pressure can be atmospheric but may also be superatmospheric in which case higher temperatures may become practicable as the volatilisation will be limited.

5

The secondary hydrolysis may be performed in a batch or continuous process. Temperature, pressure and rate of water addition can be varied. The water is preferably supplied free, that is to say not absorbed or adsorbed on a crystalline or amorphous solid support.

10

In batch operation slow addition may be typically over a period of 20 hours at room.

15 With temperature increases, pressure may have to be applied to reduce solvent evaporation. Pressure may increase the reaction rate. Higher temperatures may, it is surmised, lead to better water solubility, lower water gradients and hence desired even hydrolysis. Higher temperatures may also aid  
20 extraction of TMA from non-dissolved MAO for subsequent homogeneous hydrolysis.

The rate of water addition should preferably be slow for example less than 0.1 g H<sub>2</sub>O per liter of alumoxane (containing  
25 5 mol % of Al) obtained from primary hydrolysis per hour.

Total hydrolysis degree based on the aluminum content of the alumoxane submitted to secondary hydrolysis is from 0.05 to 0.7 mol H<sub>2</sub>O/mol Al, preferably 0.1 to 0.5, especially 0.15  
30 to 0.3. The optimum ratio depends on the history of the starting alumoxane and the optimum form of final alumoxane for a particular process which can vary with the selection of transition metal component. Formation of insoluble particles should preferably be avoided to ensure good flowability  
35 through a filter. Optimum extents or degrees of polymerisation at the end point can be determined by



polymerisation experiments and levels of unreacted aluminum alkyl. Optimum extents of hydrolysis may vary with the type of original alumoxane used for secondary hydrolysis.

- 5 For best effect it is desirable to perform the secondary hydrolysis so that fouling at the contact point of the water and alumoxane starting solution is avoided as far as possible.

10 Details of the secondary hydrolysis product

- The secondary hydrolysis product may be opaque but pumpable and stable (i.e. not prone to settling). It is believed the suspension consists predominantly of fine gels. The product  
15 if not directly used should preferably be lightly agitated and kept free of moisture, oxygen heat etc.

- The final alumoxane resulting from secondary hydrolysis may be combined with the transition metal component after hydrolysis  
20 before polymerisation. Alternatively the secondary hydrolysis may be performed on a mixture including the transition metal component and the starting alumoxane. The secondary hydrolysis may be either off-line with polymerisation (i.e. separate from the main polymerisation to produce a batch of  
25 alumoxane which has undergone secondary hydrolysis) or on-line with the actual polymerisation (i.e. before the main polymerisation but on a continuous basis producing the exact amount of alumoxane subjected to secondary hydrolysis required by the polymerisation). Some transition metal components are  
30 water-sensitive and early contact should be avoided. In such a case the secondary hydrolysis step is performed in the absence of the transition metal component.

- The effect of the secondary hydrolysis on the main alumoxane  
35 parameters is generally as follows:

Total aluminum concentration is unchanged once allowance is made for evaporated solvent; the alumoxane concentration (as determined by the difference of the total aluminum and aluminum level of unreacted aluminum alkyl) is generally higher than in the starting solution; the content of unreacted aluminum alkyl is generally from 2 to 15 mol %, and is preferably significantly lower (by 5 to 10 %) than in the starting solution; it is especially preferred that the resulting content at least half relative to the level of aluminum alkyl in the starting solution. The viscosity increases. The viscosity of a primary hydrolysis product containing 3 wt % of Al (derived from methylalumoxane and trimethylaluminum) in toluene increases at least 0.1, preferably 0.2 centistokes in viscosity, to reach a level for example from 0.9 to 1.1 or higher.

In a case of an approximately 5 % MAO solution in toluene, this can be effected by secondary hydrolysis as follows:

	Al wt%	TMA wt%	MAO wt%	$\text{Al}_{\text{TMA}}/\text{Al}_{\text{TMA}+\text{MAO}} \times 100\%$
Non-hydrolysed	2.3	2.0	3.4	30.4
Hydrolysed	2.5	1.7	3.9	25.7

The gradual hydrolysis and other process conditions are believed to contribute to an even hydrolysis, leading to an overall high hydrolysis level and a homogeneous suspension which gives a reproducible and improved performance in polymerisation.

#### Details of other aspects of invention

The invention secondly includes a process for making alumoxane which involves the above described primary hydrolysis combined with the secondary hydrolysis. At appropriate levels and treatments it becomes possible to provide a product by a

secondary hydrolysis which is storable and shippable. Preferably however the secondary hydrolysis is performed at the polymerisation site.

- 5 It is important to note that intermediate filtration steps to remove insoluble materials can in some cases be advantageously avoided by selecting appropriate conditions.

10 The invention thirdly provides a polymerisation process using the alumoxane resulting from the secondary hydrolysis described above. Advantageously the secondary hydrolysis is performed less than 2 weeks prior to the polymerisation to avoid deterioration in quality.

15 Overall the alumoxane may then be subjected to three process steps : primary hydrolysis; secondary hydrolysis and polymerisation. By interposing the secondary hydrolysis, the overall polymerisation effect becomes much more predictable and productive.

20

The secondary hydrolysis may be beneficial with a variety of polymerisation types:

25 (a) bis(cyclopentadienyl) titanium, zirconium, or hafnium compounds can be used with MAO in the widely described toluene solvent. The cyclopentadienyl rings include ones which are substituted and/or bridged.

30 (b) monocyclopentadienyl compounds using zirconium, titanium or hafnium compounds can be used with MAO in toluene solvent to make high molecular weight polymer or polymer with high comonomer levels or incorporating large comonomers (C<sub>6</sub>-C<sub>20</sub>) including higher mono-olefins and diolefins. Again the cyclopentadienyl rings may be  
35 substituted or bridged.

(c) MAO may also be used for both above types of transition metal compounds in an aliphatic solvent (See JP 2250885-A; Toyo Stauffer) where advantageously the MAO is solubilised by the use of a proportion of aluminum alkyls of the higher alkyls (C<sub>4</sub> or higher) at some stage in the preparation procedure (See JP-1258686-A; Mitsui Petrochemical).

The catalyst system may include as metallocene a compound of the general formula



wherein M is a transition metal of group IV B, V B or VI B of the Periodic Table, 66th Edition of Handbook of Chemistry and Physics CRC Press (1985-86) CAS Version, wherein R is a ligand having a conjugated electron bonded to M;

wherein L is a leaving group bonded to M and wherein Z represent one or more further conjugated ligands and/or anionic leaving groups bonded to M and/or a moiety bonded to M and to R.

The group R and optionally the group Z where Z is a conjugated ligand, may be or include a substituted or unsubstituted cycloalkadienyl group such as cyclopentadiene or a cyclopentadienyl with linked substituents such as indenyl, fluorenyl or tetrahydro-indenyl. Where at least one Z is a cycloalkadienyl conjugated group, the different cycloalkadienyl groups of R and Z may be bridged (See Exxon EP 129 368). Where one conjugated ligand group R is present and Z is not a conjugated ligand, the group R may be bridged to other transition metal ligands such as Z.

The group L and optionally the group Z where Z is an anionic leaving group may be or include an aryl group, alkyl group, an

aralkyl group, a halogen atom, a hetero atom containing ligand containing an oxygen, sulfur, nitrogen or phosphorus atom (hetero atom may be bonded to M); these groups L and Z may be connected by single or multiple  
5 bonds to M; optionally these groups may be linked to groups R or Z. Possible species are described in EP 416 815 and EP 420 436.

Polymerization may be by any method appropriate for  
10 metallocene catalysts including high pressure, solution, slurry or gas phase processes.

Examples 1-6

Starting MAO composition :

Table 1

5

Mol wt (by cryoscopy)	800 - 1200	
Al content of TMA and MAO	3 wt %	(by measuring total Al containing compounds)
Mol % TMA	See other Tables	

The secondary hydrolysis procedure

- 10 The MAO characterized in Table 1 is hydrolysed using the apparatus of Figure 1.

Nitrogen is led from container through a line 4 to a water charge pot 6. The pot is kept at a desired temperature by  
15 steam. Nitrogen gas with water vapour below the water vapour saturation level is supplied from the charge pot through a steam heated line 10 to a catalyst mixing tank 12 containing an MAO solution. The tank is agitated by a stirrer 8 and motor 9. The exhaust 14 from the tank 12 passes through a  
20 cooler 18 to condense entrained evaporated solvent. Pump 24 maintains circulation. Line 25 leads to the polymerisation reactor and more particularly the catalyst injection pump (not shown). Slow hydrolysis can be performed at a controlled temperature.

25

Polymerisation

Ethylene-1-butene copolymers were prepared at 1350 bars and at a Al/TM mole ratio near 400. TM stands for transition metal.

The polymerisations were performed in a stirred, non-cooled autoclave with downstream of the autoclave a let-down valve, a high pressure separator, a low pressure separator and a polymer removal unit such as an extruder. After polymer  
5 removal in the high pressure separator, the residue is recycled to the inlet side of a compressor system and hence returned to the autoclave. Water is injected as a catalyst killer downstream of the let-down valve. Catalyst is injected  
10 by pump at a rate so as to maintain a desired autoclave temperature profile. The concentration of residual TMA (as measured via iso-quinoline titration) prior to alumoxane treatment with more water in the secondary hydrolysis step is also indicated. The polymerisations produced liquids at low  
15 molecular weights or VLDPE's at higher molecular weight. The polymer characteristics are set out in Table 3. The secondary hydrolysis conditions and polymerisation results are shown in Table 2.

Table 2a

Example #	Reactor Temperature °C	Al/TM	mole% TMA before hydrolysis	H <sub>2</sub> O/Al mol ratio in sec hydrolysis
1 a	160	420	27	0
b	160	420	27	0.064
2 a	137	402	27.3	0
b	139	402	27.3	0.195
c	126	402	27.3	0.313
3 a	170	405	27.3	0
b	171	405	27.3	0.078
c	174	405	27.3	0.156
4 a	160	443	25.2	0
b	160	400	25.2	0.064
c	160	400	25.2	0.127
d	160	400	25.2	0.191
5 a	160	401	24.9	0
b	160	401	24.9	0.063
c	160	401	24.9	0.063
6	160	1653	100	0.22

NA: not applicable; s: slow; NR: not recorded; ref: reference



Table 2b

Example #	Hydrolysis rate gr H <sub>2</sub> O/h per 10 L	Hydrolysis T °C	Productivity PE/g cat	% Cat. Productivity increase
1 a	NA	NA	350 000	
b	s	ambient	484 000	38 over 1a
2 a	NA	NA	68 500	
b	NR	NR	103 700	51 over 2a
c	NR	NR	32 200	-53 over 2a
3 a	NA	NA	59 800	
b	s	ambient	125 000	109 over 3a
c	s	ambient	69 400	16 over 3a
4 a	NA	NA	254 000	
b	s	ambient	329 000	30 over 4a
c	s	ambient	408 000	61 over 4a
d	s	ambient	306 000	20 over 4a
5 a	NA	NA	287 000	
b	0.75	65	196 000	-32 over 5a
c	0.56	ambient	411 000	43 over 5b
6	s	ambient	45 000	

NA: not applicable; s: slow; NR : not recorded; ref: reference

Table 3a

	wt % C4 FTIR	Density gr / cc	Viscosity at 140 °C	MI
1	10.37	0.9076	NA	1.78
	10.12	0.9057	NA	1.94
2	48.95	NA	373	NA
	46.63	NA	492	NA
	55.37	NA	238	NA
3	55.29	NA	220	NA
	55.56	NA	167	NA
	54.59	NA	189	NA
4	11.48	0.9094	NA	4.82
	10.57	0.9109	NA	4.02
	11.3	0.9055	NA	5.17
	10.81	0.9061	NA	6.42
5	10.92	0.907	NA	4.82
	10.99	0.9096	NA	6.45
	10.29	0.9081	NA	6.42
6	11.85	0.9059	NA	13.66

Table 3b

	Mw GPC	MWD GPC	MIR
1			15.06
			16.58
2	5332	4.21	
	6389	5.17	
	4377	6.12	
3	4497	2.1	
	4014	2.17	
	3734	2.33	
4	65800	2.64	
	73800	2.4	
	67600	2.76	
	62400	2.33	
5	65800	2.64	
	56490	2.73	
	62400	2.33	
6			17.97

25

Viscosity was determined according to ASTM-D MI and MIR were determined according to ASTM-D-1238; condition E.

Example 1 used bis(tetrahydroindenyl)dimethylsilylzirconium  
5 dichloride ( $\text{SiMe}_2(\text{H}_4\text{Ind})_2 \text{ZrCl}_2$ ) as TM catalyst component. It shows an increase of circa 38 % in catalyst productivity upon secondary hydrolysis at an  $\text{H}_2\text{O}/\text{Al}$  molar ratio of 0.064.

Example 2 uses bis (methylcyclopentadienyl)zirconium  
10 dichloride.

Examples 3 to 6 use the same metallocene as Example 1.

Examples 2-4 show that an optimum  $\text{H}_2\text{O}/\text{Al}$  mole ratio exists for  
15 the secondary hydrolysis. Above that optimum ratio, the catalyst productivity decreases. For the catalyst  $\text{SiMe}_2(\text{H}_4\text{Ind})_2\text{ZrCl}_2$ , this optimum is around 0.1 mol  $\text{H}_2\text{O}/\text{mol Al}$  with most MAO types. The total hydrolysis level of the MAO may be around 0.6  $\text{H}_2\text{O}/\text{Al}$  (molar).  
20

In Example 5, the negative effect of hydrolysing too rapidly at high temperature (65 °C) compared to ambient temperature (15-25 °C) on productivity of  $\text{SiMe}_2(\text{H}_4\text{Ind})_2\text{ZrCl}_2$  is shown.

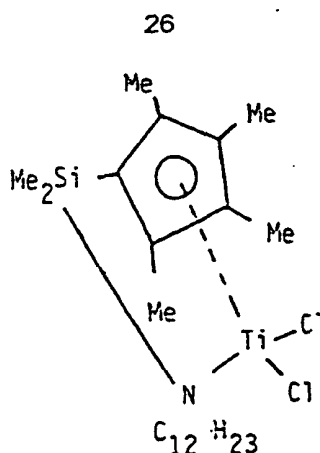
25 In Example 6, pure TMA was hydrolysed at a 0.22  $\text{H}_2\text{O}/\text{Al}$  ratio. A low catalyst productivity (45,000 gr PE/gr TM) and high MI were obtained.

#### Example 7

30

As cocatalyst there was used a separately prepared MAO solution in toluene, hydrolysed to provide a viscous opaque suspension and then combined with a transition metal catalyst before polymerisation. The catalyst has the formula:

35



The starting MAO solution had the composition of Table 1.

The TMA and MAO in Table 5 are calculated as explained previously.

Secondary hydrolysis was generally as in the previous Examples subject to the additional details in Table 4 :

Temp. 60 - 70 deg C;

H<sub>2</sub>O addition at 0.2 H<sub>2</sub>O per mol Al; and

a hydrolysis period of 12 - 24 hrs.

Polymerisation was performed at the conditions shown in Table 4, generally using water as killer injected at mol ratio of 0.075 - 0.22 H<sub>2</sub>O/Al downstream of the polymerisation. The polymerisation occurred in an autoclave as used in the earlier examples with the temperature gradually increasing to the outlet; the temperature in the middle of the autoclave is indicated in Table 4. The pressure was 1300 bar. Hydrogen was injected in the amounts indicated to achieve the indicated product MI. Enough comonomer was added to reach the wt% comonomer and density values indicated. The residence time was from 60 to 70 seconds. Butene-1 was used as comonomer.

Table 4

Example	Reactor Temperature	H <sub>2</sub> ltr/min	Catalyst (1) ml/hr	TM gr/ltr	Al/TM mol/mol
A	158	0.10	1000	0.24	1389
B	160	0.15	400	0.24	1389
C	160	0.15	430	0.24	1389
D	160	0.15	320	0.24	1389
E	160	0.07	180	0.24	1458
F	150	0.09	1000	0.24	1492
G	160	0.09	270	0.24	1492
H	160	0.3	1000	0.24	1418
I	160	0.15	140	0.24	1418
J	160	0.15	90	0.95	358

Ex.	Type/degree of treatment	Hydrol temp. °C		H <sub>2</sub> O/Al (2) hydrol	Starting TMA mol %	Final Mol % TMA
A	unhydrol.		High TMA-MAO ratio	0	47	8-10%
B	hydrol.	ambien t	Same MAO, stable operation	0.55	46	
C	hydrol.	ambien t	Very high level of hydrolysis	0.61	46	
D	Hydrl + 5d60C	ambien t	5 days soaking at 60°C prior to secondary hydrolysis	0.3	46	
E	hydrol.	ambien t		0.19	26	
F	unhydrol.			0	15	
G	hydrol.	ambien t		0.06	15	
H	hydrol.	ambien t	Fast hydrolysis < 4 hrs.= bad cat.	0.29	27	
I	hydrol.	60	Very slow hydrolysis best MAO tested	0.18	27	
J	hydrol.	60	Reduced Al/TM ratio	0.18	27	

Example	MI 2.2 (5)	MI Ratic	wt % comonome r	density gr/ml	Producti vity PE/Cat. (3)	Produc tivity PE/MAO (4)
A	5.0	17.0	14		54167	295
B	15.0	30.0	23	0.8950	177083	966
C	13.0	31.0	25	0.8900	164729	899
D	2.0	29.0	34	0.8750	221354	1207
E	0.5		40		393519	2146
F	10.0	29.0	31	0.8830	50000	273
G	1.1	28.0	42		262346	1431
H	2.2				50000	273
I	0.9	23	38	0.8640	505952	2760
J	0.9	24	39	0.8640	163743	3535

29

- (1) 1000 ml/hr is the maximum pumping rate, indicative of poor catalyst performance;
- (2) This is the secondary hydrolysis ratio
- (3) Calculated on g of PE per gram of metallocene compound  
5 on a 1 minute residence time
- (4) Calculated on g of PE per gram of Al containing compound per 1 minute residence time
- (5) Determined according to ASTM-D-1238 Condition E

#### 10 Advantages

The invention permits efficient use of TMA in making MAO in an economic manner with high overall yield and high overall activity. Amounts of TMA or volatile aluminum alkyl can be  
15 kept low. The invention does not detract from killing efficiency based on the use of water as described in PCT/EP 9200377. Cyclopentadienyl compounds sensitive to the presence of unreacted aluminum alkyls especially TMA such as monocyclopentadienyl compounds and/or mono or bis  
20 cyclopentadienyl titanium based compounds and/or compounds having strong electron-donating ligands on the metal such as amido groups, may be used with MAO prepared according to the invention. Controlled post-hydrolysis conditions and success criteria are set out.

25

It is believed that the method of the invention has the effect of "normalising" MAO prepared on an industrial scale so that its performance is much more predictable. The methods work with underhydrolysed MAO solutions and MAO solutions which  
30 have been properly hydrolysed but then treated to remove solid MAO particles or gels. In spite of an absence of clear structural characteristics which can be identified, significantly improved cocatalytic performance can be achieved in a repeatable manner which adds only slightly to  
35 overall cost.

It is believed that the secondary hydrolysis reduces TMA levels and levels of low oligomers transforming them into catalytically useful species without unduly impacting the level of effectiveness of higher oligomers. The residual TMA  
5 levels may help to maintain solubilisation or suspension stability of secondary hydrolysed MAO. Low TMA levels also help in achieving a narrow molecular weight distribution.

Removal of TMA by distillation on its own or filtration of  
10 solid MAO are not as beneficial because potential source materials for effective MAO are removed.

The lower TMA levels also reduce transfer activity in polymerisation and help to increase the average molecular  
15 weight.

Whilst the preferred alumoxane species, MAO, has been studied analogous effects may be expected with alumoxanes using starting materials other than trimethylaluminum.



CLAIMS:

1. A method of producing alumoxane which comprises  
5       subjecting an alumoxane to a secondary hydrolysis by:  
  
      hydrolysing an alumoxane starting solution or suspension  
      which has an initial viscosity at a normalised  
      concentration of 3 wt% Al in such a manner as to produce  
10       a substantially stable suspension having a final  
      viscosity at least 0.1 centistoke preferably 0.2  
      centistoke above the initial viscosity.
2. A method according to claim 1 which the alumoxane is  
15       methylalumoxane.
3. A method according to claim 1 or claim 2 in which the  
      starting alumoxane solution contains unreacted aluminum  
      alkyl and in which the secondary hydrolysis reduces the  
20       aluminum alkyl content by at least 50 %, relative to the  
      level in the starting alumoxane solution preferably to a  
      level of from 2 to 15 mol % of aluminum alkyl in the  
      suspension.
- 25   4. Method according to any of the preceding claims in which  
      the suspension has a viscosity of at least 0.5 centistoke  
      greater than that of the starting solution and/or passes  
      an 0.5 mm pore filter without clogging.
- 30   5. Method according to any of the preceding claims in which  
      the difference between the final viscosity and the  
      initial viscosity exceeds the difference between the  
      initial viscosity and the viscosity of the solvent on its  
      own.
- 35   6. Alumoxane suspension which is stable in a solvent medium,  
      said suspension having a viscosity of from 1.0 centistoke

to 10 centistoke when normalised to a concentration of Al-containing compounds of 3 wt%? preferably containing from 2 to 15 mol % of an unreacted aluminum trialkyl.

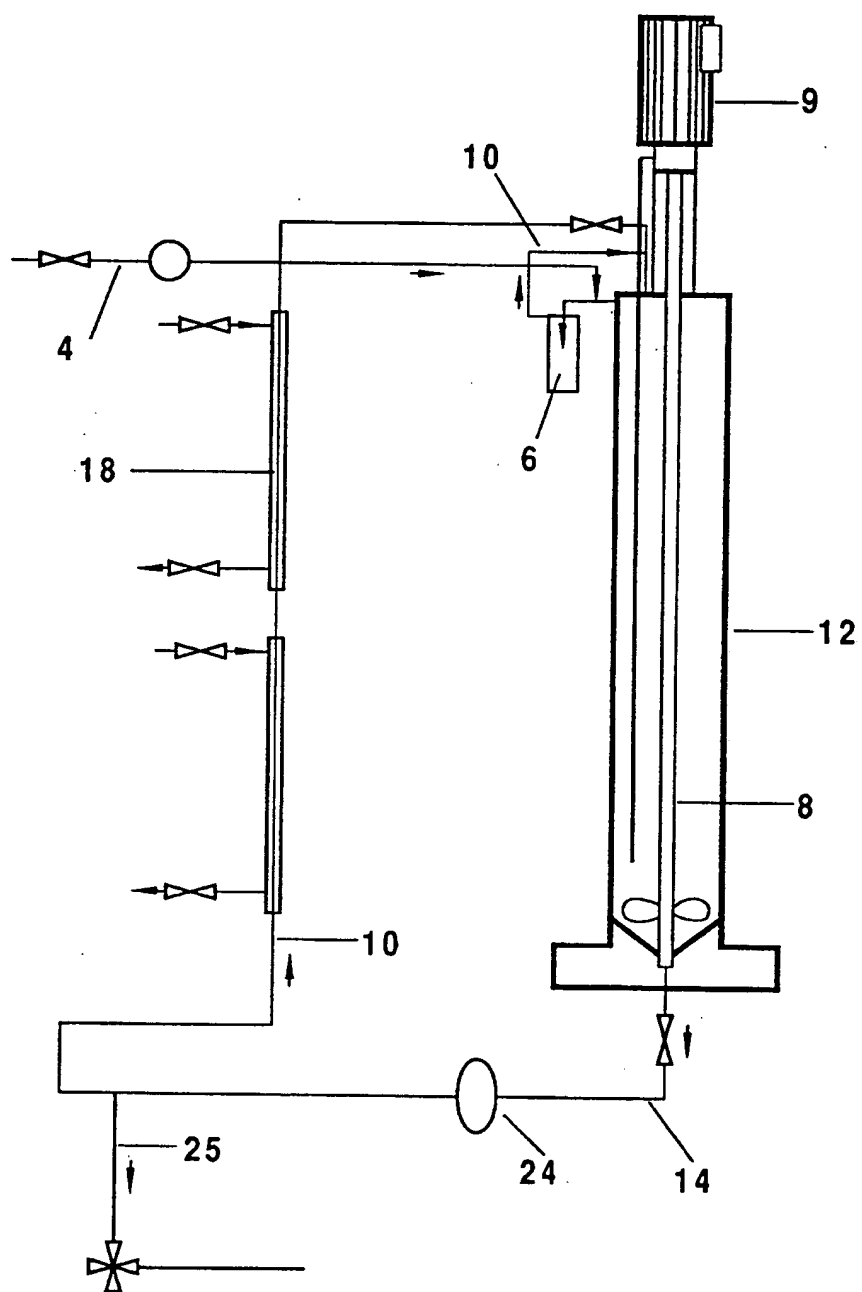
- 5 7. A method of preparing alumoxane which comprises using a product obtained from a primary hydrolysis of an aluminum alkyl to provide a macroscopically clear solution having an initial viscosity as a starting material for a secondary hydrolysis to produce a substantially stable, opaque suspension having a final viscosity above the initial viscosity.
- 10
8. A method according to claim 7 in which the secondary hydrolysis is performed by adding water at a rate of less than 0.1 g of H<sub>2</sub>O per liter of alumoxane solution obtained from primary hydrolysis per hour.
- 15
9. A method according to claim 7 in which the solvent comprises toluene.
- 20
10. A method according to any of claims 7 to 9 in which at least the final 0.05 mol of H<sub>2</sub>O per mol of Al, preferably the final 0.1 mol are added at a rate of less than 0.03 preferably less than 0.01 mol of H<sub>2</sub>O per mol of Al per hour at from 0 to 50 °C.
- 25
11. A process for polymerising an olefin involving injecting the alumoxane suspension obtained from a method according to any of the preceding claims in association with a transition metal component into a polymerisation reactor, the secondary hydrolysis having been performed such that the catalyst productivity in grams of olefin polymer per gram catalyst transition metal compound is higher than that using the starting alumoxane not subjected to secondary hydrolysis.
- 30
- 35

33

12. A process according to claim 11 in which the pressure is from 200 to 2500 bar in a bulk phase.

1/1

FIGURE 1



# INTERNATIONAL SEARCH REPORT

Inter nal Application No  
PCT/EP 94/00633

A. CLASSIFICATION OF SUBJECT MATTER  
IPC 5 C07F5/06 C08F10/00 C08F4/602

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
IPC 5 C07F C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO,A,92 21685 (AKZO CHEMICALS INC.) 10 December 1992 see the whole document ---	1
A	EP,A,0 405 221 (ETHYL CORPORATION) 2 January 1991 cited in the application see the whole document ---	1
A	EP,A,0 328 348 (MITSUI PETROCHEMICAL INDUSTRIES, LTD.) 16 August 1989 cited in the application see the whole document ---	1
A	US,A,3 954 958 (MATSUI, A. ET AL.) 4 May 1976 see the whole document -----	1

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

19 May 1994

Date of mailing of the international search report

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# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP 94/00633

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